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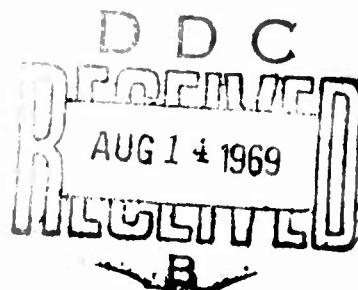USAAVLABS ltr 23 Jun 1971

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USAAVLABS TECHNICAL REPORT 69-5

FEASIBILITY OF DETECTING IMPENDING FATIGUE FAILURE IN METALS BY OBSERVATION OF SURFACE CHEMICAL AND PHYSICAL PHENOMENA

By

Phillip J. Joseph

April 1969

U. S. ARMY AVIATION MATERIEL LABORATORIES
FORT EUSTIS, VIRGINIA

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USAAVLABS Technical Report 69-5
TITLE: Feasibility of Detecting Impending Fatigue Failure in Metals
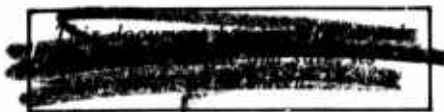By Observation of Surface Chemical and Physical Phenomena

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DEPARTMENT OF THE ARMY
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FORT EUSTIS. VIRGINIA 23604

This report represents the results of one of several investigations
being conducted by this Command to determine the feasibility of de-
tecting impending fatigue failures. Techniques being investigated in
addition to the one reported herein are: measurement of changes in
surface topography by using optical correlation between stressed and
unstressed surfaces (autocorrelation), measurement of the ability of
material to retain or absorb an inert gas as the material undergoes
fatigue cycling (kryptonation), and measurement or monitoring of the
small changes in electromagnetic properties of materials as grain
slippage or strain hardening occur as a function of fatigue cycling
(inductive sensing).

This command concurs with the findings of the contractor.

Task 1F162203A43405
Contract DAAJ02-68-C-0025
USAAVLABS Technical Report 69-5

April 1969

FEASIBILITY OF DETECTING IMPENDING FATIGUE FAILURE IN METALS BY OBSERVATION OF SURFACE CHEMICAL AND PHYSICAL PHENOMENA

Summary Technical Report

CAL Report NM-2555-P-1

By

Phillip J. Joseph

Prepared by

Cornell Aeronautical Laboratory, Inc.
Buffalo, New York

for

U.S. ARMY AVIATION MATERIEL LABORATORIES
FORT EUSTIS, VIRGINIA

ABSTRACT

The purpose of the study was to investigate, through laboratory tests, the potential for developing fatigue indicators for which some merit was evident from prior research. The response of photographic emulsions, phosphor coatings, and chemical indicator coatings to physical and surface-chemical reactions associated with fatigue damage in 2024-T3 aluminum was investigated. Many indicators were examined for their ability to meet the Army's requirements (1) under field conditions, (2) for long periods, and (3) for detection of damage that is characteristic of both high- and low-stress cycling. None of the candidate indicators was developed to a point where it showed promise for meeting these requirements during the contract period. Further investigation is recommended for one color indicator that was only briefly tested. Surface replication followed by microscopic examination was found to provide useful information on progressing fatigue damage, and effort directed toward developing practical methods for relating replica data to remaining life-to-failure is recommended.

FOREWORD

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INTRODUCTION

A great need exists for a fatigue-damage detection and monitoring
system capable of predicting the remaining service life of a part for
purposes of safe but economical replacement. To meet this need,
the Army Aviation Materiel Laboratories decided to investigate,
through laboratory tests, the suitability of a number of fatigue
indicators for which some potential was evident from prior investigations. This report describes research on several techniques,
based on surface-chemical phenomena. Those techniques which
appeared to have the greatest potential for future field use received
the most attention. Three methods were selected which might respond
to exo-electron emission or, more specifically, to the hydrogen
peroxide formed at active sites of surface fatigue damage where slip
bands and microcracks have developed. The three methods investigated employed photographic emulsions, phosphor coatings, and
chemical indicator coatings.

The techniques showing the most promise would be developed into a
suitable package for extensive fatigue tests designed to determine the
correlation between indicator response and actual fatigue damage. A
surface replication technique employing microscopic observation would
serve as an independent control in assessing surface fatigue damage.

Our intensive investigation of numerous indicator schemes did not lead
to a method that would meet the Army's need for eventual applicability
(1) under field conditions, (2) for long periods of time, and (3) for
detection of damage that is characteristic of high- and low-stress cycling.
Hence, we do not recommend further development of schemes based on
exo-electron and related surface-chemical effects. We did find, however,
that surface replication followed by microscopic examination does provide much useful information on the state of surface damage of a material
undergoing fatigue stress. Consequently, effort directed toward developing practical methods for relating replica observations to remaining
life-to-failure is recommended.

PROGRAM APPROACH

Our original program called for the testing and development of three
different techniques having response possibilities useful in detecting
or monitoring exo-electron activity or related surface effects. Of the
three methods, only one or two whose output response to fatigue damage
showed some degree of correlation would receive further package de-
velopment. These developed packaged systems would then be subjected
to fatigue tests with metal specimens under a variety of stress conditions
to establish more generally and quantitatively the degree of useful
correlation.

As actually conducted, the program concentrated on exploration of a
large number of indicators, all based on the three methods planned at
the outset. The originally planned comprehensive indicator-fatigue life
correlation test was replaced by a series of short tests in which the
pertinent features of candidate indicators were determined.

In Figure 1 the entire investigation is represented in a program flow
diagram. Fatigue tests were conducted at the three levels shown on
the figure: 35,000 psi (100,000-cycle life), 26,000 psi (500,000-cycle
life), and 24,000 psi (1,500,000-cycle life). In order to conserve time,
our screening tests were run at the high stress level. Therefore most
activity is indicated inside the 35,000-psi block. The small boxes in a
horizontal line near the top of the diagram represent the three indicator
methods that were explored: phosphors, Russell photograpl.y and
chemical indicators. Of these, the latter were investigated most
extensively, as can be seen by the entries on the right side of the diagram.
Our report follows the diagram flow lines, and the diagram titles also
head the sections of the report.

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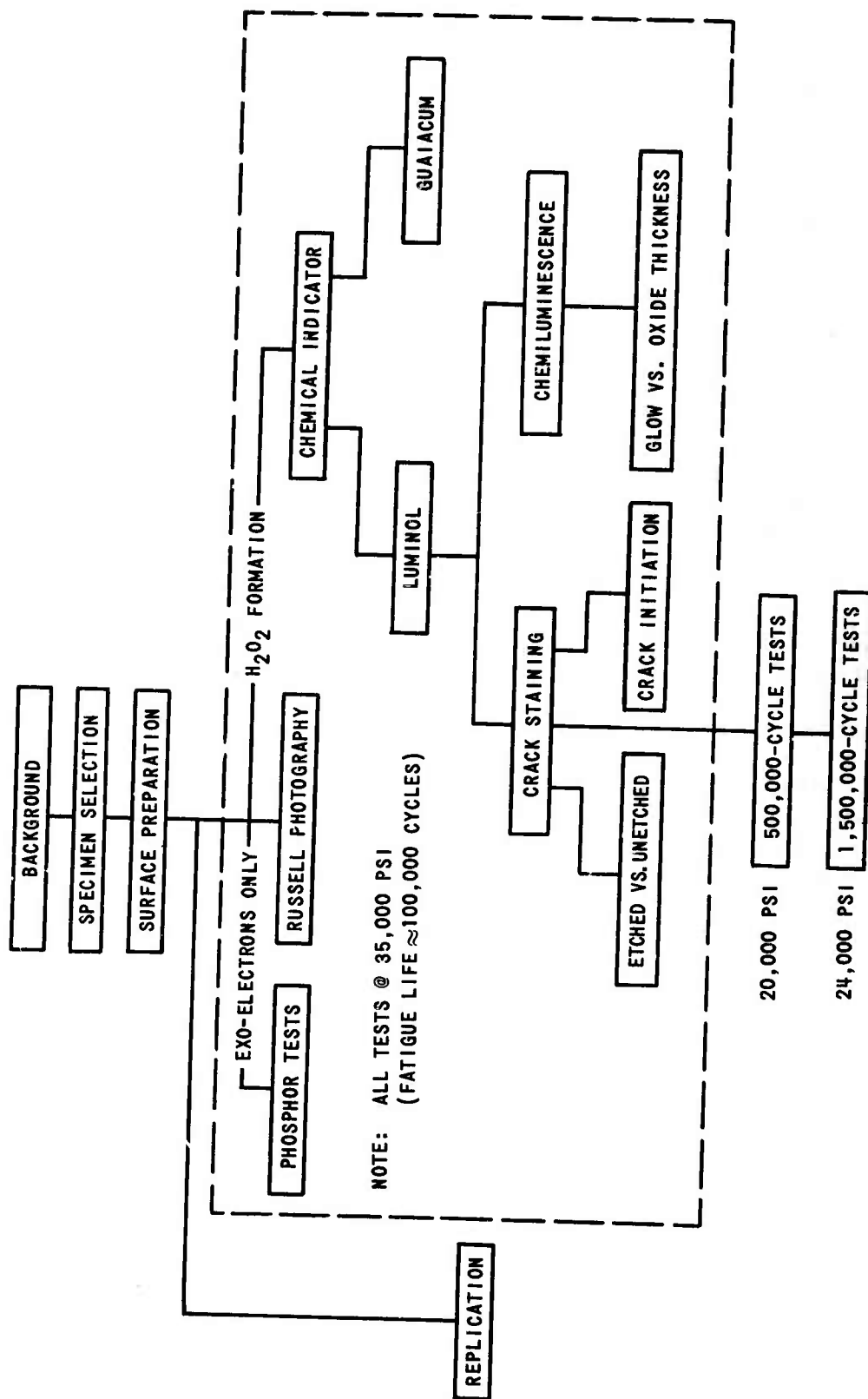
Figure 1. PROGRAM FLOW DIAGRAM - FATIGUE INDICATOR STUDY.

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BACKGROUND OF THE RUSSELL EFFECT AND
THE EXO-ELECTRON PHENOMENON

Historically, these two effects were discovered independently and at
different times; however, they are believed to be related phenomena.
The older of the two refers to the ability of fresh or abraded metal to
produce a latent image on a photographic emulsion. Although this
effect was observed as early as 1842 by Moser (1) and various others (2),
it is now referred to as the "Russell effect" due to Russell's extensive
work with it.(3) He found in 1897 that in the presence of moisture (4),
many metals when scratched or fractured produced a corresponding
latent image on a photographic plate in contact or in the near vicinity.
Russell found that the agent responsible for the darkening of the
emulsion was hydrogen peroxide, a finding also confirmed by many
others.(5, 6) Actually Traube in 1893 found that H_2O_2 was produced
in small quantities when certain metals (Zn, Mg, and Al) in finely
divided form were shaken with water containing dissolved oxygen.(7)
Others later reported similar reactions for other metals and attributed
the effect to "auto-oxidation". (7) This was thought to be a process in
which the slow oxidation of the metal would simultaneously cause the
oxidation of the H_2O molecules to H_2O_2. (7)

The Russell effect has been studied more recently by means of a
technique known as "autoradiography". Melaka and Barr, using this
technique with strained, pure-zinc single crystals, were able to show,
on high-resolution stripping emulsion, that the Russell effect occurs at
the slip bands of a plastically deformed metal.(8) Using the same
technique, Grosskreutz found similar evidence with fatigued poly-
crystalline aluminum. He also found that fatigue cracks were especially
effective in producing H_2O_2 in their early stages of growth.(9)

Abnormal electron emission activity from fresh or worked metal surfaces
was first encountered with freshly manufactured Geiger-Muller counter
tubes. Scratched or abraded surfaces were effective sources of this
effect, which decayed with time.(10) Kramer extensively investigated
this effect using point counters during the 1940's and published his
findings in 1950. Kramer theorized that an exo-thermal phase trans-
formation at the metal surface was responsible for the emission; hence,
the term "exo-electron" was introduced. Although this hypothesis is.
no longer held, the term exo-electron was retained by agreement of
workers in this field at a symposium in 1956. The term exo-electron is
applied to electron emission processes that are structure dependent,
regardless of the means of excitation in the emitting material.(10, 11)
The various electron emission phemonena can be classified according
to the mode of excitation and stimulation. Bohun, in his comprehensive

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review article, discusses the various emission phenomena in terms of
this means of classification.(11) The phenomena of particular interest
to this project were plasto-stimulated, co- and post-electron emission
(the simultaneous and delayed electron emission from plastically de-
formed material undergoing chemical oxidation). Such deformation
occurs with metals during fatigue.

More recently Krogstad and Moss studied plasto-stimulated, co- and
post-electron emission from fatiguing metals by cyclically torsion-
loading them under vacuum. They found that emission events occurred
during each strain cycle, being negligible during the initial part of the
fatigue life and increasing to a maximum at about 1/3 the fatigue life,
followed by a slow decrease until failure. These results were typical
of iron, titanium, nickel, and gold. They reported no emission from
aluminum.(2) Grosskreutz and Benson reported similar findings with
aluminum when subjected to tensile strain in a clean vacuum.(3)
Gieroszynski and Sujak reported electron emission from strained
aluminum in a vacuum, although only with anodized oxide layers thicker
than 500 $\overset{o}{A}$. They believe the electrons in this case are emitted from
the oxide layer, in particular from the walls of microcracks in the oxide
layer which are charged as the result of the deformation or separation
of the dielectric oxide during the opening of a crack. In vacuum,
the electric field set up in the fissure by this effect could cause local
field emission of electrons.(12) It appears, then, that aluminum will
not emit pure plasto-stimulated electrons unless it is anodized into an
oxide layer thicker than 500 $\overset{o}{A}$.

As mentioned before, the Russell effect is believed by many researchers
to be directly related to, or caused by, exo-electron emission.(13, 8, 9, 2)
Since exo-electron emission from abraded aluminum in a vacuum is
known to depend on the presence of small amounts of oxygen (a chemi-
stimulated emission process) and the Russell effect(at atmospheric
pressure) also depends on the presence of oxygen and water vapor, a
similarity between these two effects is very evident. Whether the H_2O_2
is produced directly by exo-electron interaction with oxygen and water
molecules or by some other reaction at the surface (e. g.,"auto-oxidation"),
the reaction site probably is the same; i. e., fresh metal is exposed at
slip bands and/or microcracks. Thus, it seems possible that slip band
and microcrack growth can be monitored by means of the Russell effect.

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SPECIMEN AND FATIGUE TESTER CONSIDERATIONS

SELECTION OF MATERIALS

The alloy studied was 2024-T3 aluminum. Our selection was influenced
by the availability of fatigue data on this alloy, its use in aircraft
components, and the fact that a "Russell effect" could be expected
from aluminum.(14, 4, 6) This aluminum alloy has an ultimate
tensile strength of 64,000 psi. The highest of three stress levels
chosen for indicator tests was 35,000 psi, giving a corresponding
nominal fatigue life of 100,000 cycles. As an upper bound, these
values were well within the region of true fatigue, and allowed our test
times to be minimized for preliminary screening tests. Other stress
levels used were 26,000 and 24,000 psi with nominal fatigue lives of
500,000 and 2,000,000 cycles, respectively. The specimen geometry
(Figure 2) used for these tests was determined by load capabilities of
our fatigue machine and by the 0.126 in. material thickness chosen.

SURFACE PREPARATION

2024-T3 sheet stock from which the specimens were made was carefully
selected to avoid scratches and other surface flaws. After cutting and
machining, the specimens were further selected to avoid even small
scratches in the high-stress area. Those specimens used initially for
fatigue tests were cleaned thoroughly with solvent (methanol) only. As
pointed out earlier in this report, any significant plasto-stimulated
electron emission from aluminum would require an oxide layer thicker
than 500 Å.(12) Because the phosphor tests would require actual
electron emission and it was not known how H_2O_2 production would
depend on oxide thickness, it was decided that specimens with oxide
layers of controlled thickness should be used. Thick oxide layers
formed by the anodization process required an etched or electropolished
initial surface.

We tried two surface treatment techniques, electropolishing and chemical
etching, to determine which technique would give our 2024-T3 aluminum
specimens a smooth and uniform surface prior to anodization. Chemical
etching was selected as the better technique, since severe flow marks
due to preferential etching resulted from electropolishing. *

The chemical etching process consisted of an etch with 1% KOH solution
followed by a treatment with a 50% nitric acid solution. The second
treatment is required to remove the sludge-like coating that forms on

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* Later in the project, replication - microscopy crack studies required
smooth electropolished surfaces; efforts to electropolish small
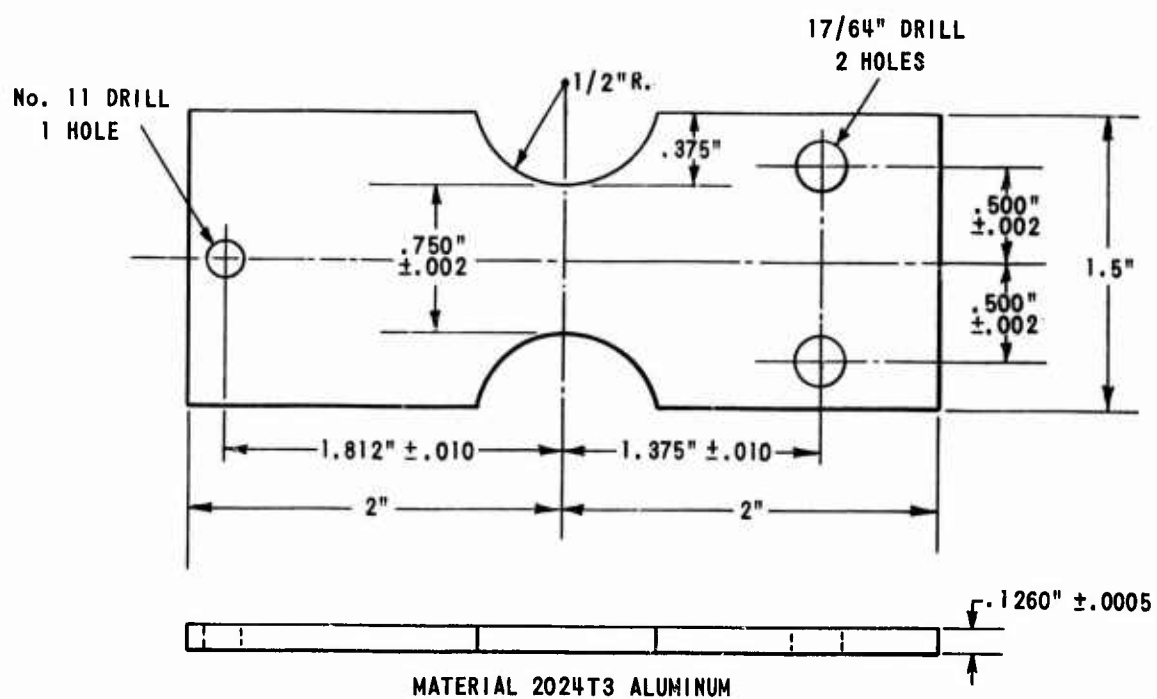areas of etched specimens were successful.

Figure 2. FATIGUE SPECIMEN (FULL SIZE).

our alloy because copper, manganese and other constituents of this alloy are insoluble in the alkali etch. Solvent-cleaned specimens were first etched for two to three minutes in the KOH solution at 76° F (average temperature), washed and dipped in the HNO_3 solution, followed by rubbing with an HNO_3-soaked cotton swab. These steps were repeated until ten minutes of KOH etch time was accumulated, resulting in a reduction of about .0001 in. in specimen thickness. At this stage the specimen surface had a uniform matte appearance. The final rinse was made with distilled water.

The freshly etched aluminum specimens were next anodized at room temperature in a 25% (by weight) citric acid solution. The resulting thickness, D, of the anodized oxide layer depends on the applied, or formation, voltage in the following way:

$$D = 14 \, V_f$$

where V_f is the formation voltage and D is given in Angstrom units.(11, 14) At a set voltage the oxide layer will grow until it has reached a thickness equal to 14 Å per applied volt of potential; at that point the anodizing current levels off to a small leakage value.

The cited relationship between oxide thickness and formation voltage was known to hold for pure aluminum and was verified for our 2024-T3 alloy by measurement; the oxide thickness of several anodized specimens was checked by means of a stripping-replica, electron microscopy technique similar to one developed by Doherty and Davis.(15) The stripping technique required that the anodized specimen be heated in an argon atmosphere to about 500° C and quenched in liquid nitrogen. The bond between the aluminum metal and the oxide interface is weakened locally due to the formation of small surface pits at the metal-metal oxide interface. This presumably comes about due to a clustering or condensation of vacancies when the vacancy-saturated material is quench-cooled. Also, the rapid chill to -195° C should cause cracking of the oxide as the result of the large differential thermal contraction. Such local oxide patches strip off when a surface plastic replica is made. An electron microscope specimen was prepared from this replica by shadowing the adhering oxide platelets with metal, and the thickness of the oxide was determined from the observed shadow dimensions. The results showed good qualitative agreement with the anodizing voltage-thickness relationship.

Specimens were prepared with the following oxide thicknesses: 200 Å, 500 Å, 700 Å, 1000 Å, 1500 Å, 2000 Å, 2500 Å, and 3000 Å.

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PRELIMINARY FATIGUE TESTS

A Sonntag-Model SF-2 flexure fatigue testing machine was used for all fatigue tests. This machine produces a constant alternating force by means of an adjustable, unbalanced rotating mass. The specimen is held between fixed and movable clamps, one of them having an arm connected to an oscillating load yoke. Thus the specimen is loaded cyclically in cantilever fashion. Flexure frequency is 1800 cycles per minute.

Prior to fatigue tests, the machine was calibrated by tuning the system for resonance and determining the accuracy of the alternating force that can be set on the machine. Resonant tuning of our machine is necessary because it is equipped with a compensating spring that absorbs all unwanted forces produced by the reciprocating masses at this resonant frequency. Otherwise these inertial forces would be transmitted to the specimen. The alternating force that the machine applies to the specimen is normally set by altering the moment arm of the rotating eccentric in the oscillator cage; this force may be set to the nearest tenth of a pound. To check this scale calibration, the force delivered to the specimen was measured by independent means; i.e., by comparing specimen deflections obtained from known static loads with those obtained dynamically with the machine. Machine load settings were found to require a scale correction amounting to 4.5%. We concluded that the alternating force applied to the specimen can be reliably determined to within 4%. Therefore, stresses in the material are accurate to that same level, assuming constancy of specimen shape.

Following calibration of the flexure fatigue testing machine, preliminary bending tests were performed, and the S/N curve for aluminum alloy 2024-T3 was determined by plotting the dependence of specimen life in number of cycles to failure, N, on the maximum applied stress, S (Figure 3). Most of the plotted points are the average of three tests at the same stress, showing the average deviation as error bars. The points corresponding to low stress and long specimen life were not made in triplicate due to the extremely long test times involved. Points at less than 60,000 psi stress would be too close to the static failure point of 2024-T3 aluminum to be of interest in fatigue tests. The specimens of the second test series were machined with a smoother surface finish than those of the first series. This difference in surface smoothness in the notched area had some effect on fatigue life. All specimens used thereafter had this smoother surface finish. The results obtained with the two finishes are indicated separately in Figure 3.
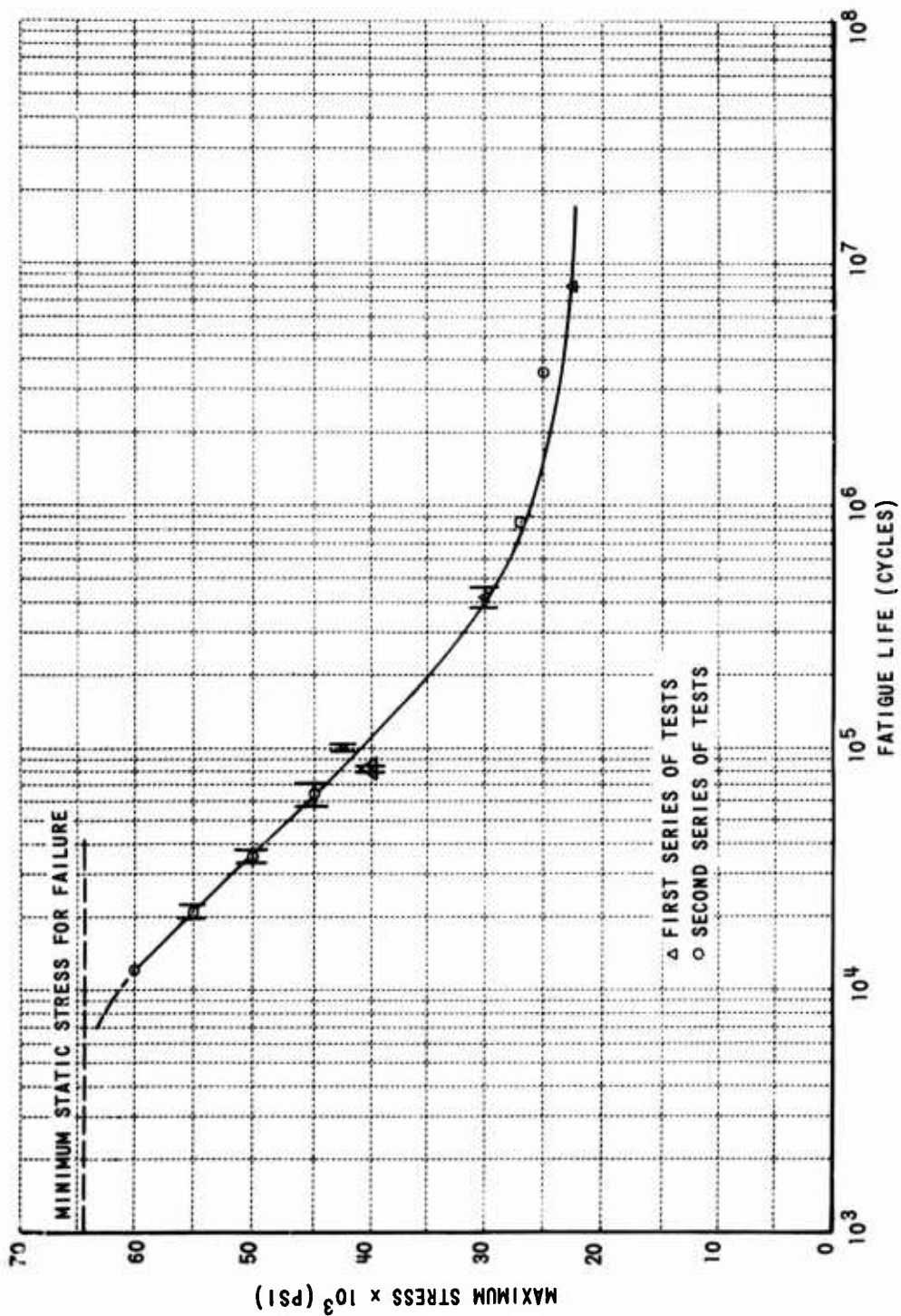
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Figure 3. S/N CURVE FOR 2024-T3 ALUMINUM ALLOY.

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RUSSELL PHOTOGRAPHY

"Russell photographs " and autoradiograms of the type referred to by Grosskreutz (3, 9) are based on the blackening of a photo emulsion by H_2O_2 . Photographic emulsions are sensitive detectors of H_2O_2 since, according to Russell, the vapor from a solution containing one part of H_2O_2 per 1,000,000 parts of H_2O will produce a latent image on a photographic plate in about 18 hours. (4)

The following discussion is given in some detail due to the uncommon procedures involved. An autoradiograph technique first reported by Grosskreutz (3) was tried initially, as it was known to work. A strippable emulsion, Kodak AR10, was used. The emulsion had to be removed from the glass plate by gradual immersion in water. The only 15 μ thick emulsion which floats on the water surface must be lifted up carefully after the metal specimen is immersed under it. When dried, the emulsion adheres to the specimen surface rather well. Except for the brief use of a dim safe light (Wratten Series 2), this work must be done as nearly as possible in complete darkness. Prior to covering with emulsion, the metal specimen was severely abraded with a scraping tool. After an 18-hour exposure, the emulsion-coated specimen was developed and fixed with both in intimate contact. After washing, the emulsion was stripped or floated from the specimen. The developed emulsion showed the type of fine detail, grain texture, and spots where areas were severely deformed that are claimed for this method.

This technique, however, is a difficult one because of the delicacy and skill required. Also, since the emulsion requires development while it is attached to the metal under test, the technique was judged unsuitable for a package system.

It appeared, however, that the technique first used by Russell would meet program development requirements since intimate contact of the emulsion and metal surface is not necessary. Although this method does not have the full resolution of surface detail of the strippable emulsion method, it can be carried out with photographic strip film - a considerable convenience. Several photographic emulsions were tried in order to determine the best material and procedure for Russell-photo studies and indicator package development.

These tests were made with photographic films of various emulsion types on freshly abraded aluminum alloy 2024-T3 specimens. As shown in Figure 4, these emulsions were all taped to a single glass plate and supported, emulsion side down, 1/16 in. above the abraded metal surface to insure identical test conditions.
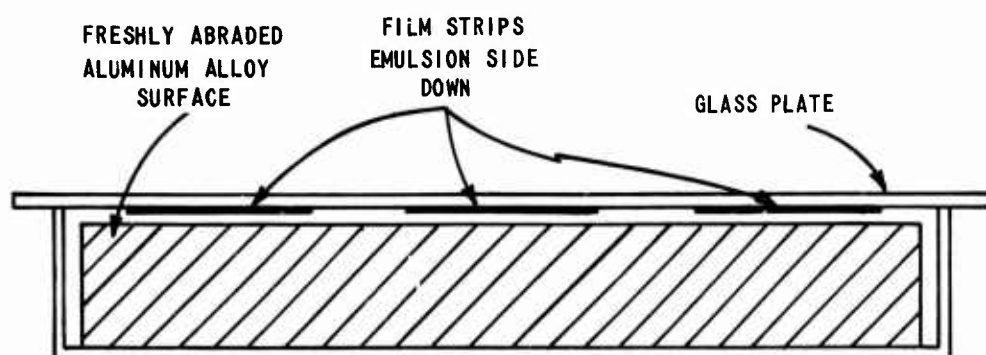
11

Figure 4. MULTIPLE EMULSION TEST CONFIGURATION.

Positive results were obtained when relative humidity was increased to 100%. Film darkening (by H_2O_2) apparently followed the same reciprocity-law behavior as that found with exposure to light. Thus, an emulsion sensitive to very low light levels, due to low reciprocity-law failure, was found most satisfactory. Such an emulsion is Kodak 103 a-O, designed for use in astronomy, where long exposures to low light levels are the rule.

Following the preliminary test of freshly abraded aluminum surfaces, fatigue tests were conducted with oxide-coated specimens after they had been cyclically stressed to about 60% of their fatigue life. The specimens were then placed, together with film, in a moisture- and light-tight container with a water-moistened pad to maintain 100% humidity conditions. Figure 5 shows the film and specimen configuration. Film was exposed to both the top and bottom of the specimen; the films were held to the glass plates by double-coated Scotch tape and placed with the emulsion side 0.015 in. from the specimen surface by means of spacers. Exposures were made for 18 to 20 hours.

The results of the work showed a weak and poorly reproducible effect in the areas of the specimen where maximum stress existed during the fatigue tests. This weakness of the effect was thought to be due to the fact that with our type of fatiguing process (flexure method), the micro-cracks are closed when the specimen is in its relaxed position. To keep the cracks open during the film exposure tests a fixture was constructed (see Figure 6) which holds the specimen to the maximum bend radius that is experienced during each flexing cycle of the fatigue process. The 103 a-O 35-mm film fitted in the slots formed between recesses cut into the top clamp plates and the specimen. Specimen surface and emulsion were in close contact during the exposure. The device was successful in that a consistent Russell-type latent image occurred in the curved area. However, since the film was also exposed to the oxidation effects of the metal of which the fixture is comprised, corrosion of various parts of the fixture did occur under the 100% humidity conditions. To overcome this problem the specimen geometry was changed. The new specimen geometry had the same overall dimensions except for the substitution of a central hole .980 in. dia. in place of the constriction formed by external, curved indentations. Fatigue life was virtually the same for both geometries. This new configuration enabled us to restrict the H_2O_2 - emulsion effect to a smaller, bounded area of the film and to eliminate the effect of background metal (bending fixture parts) by sealing off the bottom portion of the hole with a plastic cover and the top with the film itself. A clean paper pad moistened with a drop of distilled water was sealed in the closed cavity during the Russell exposure to supply the moisture necessary for the production of H_2O_2.

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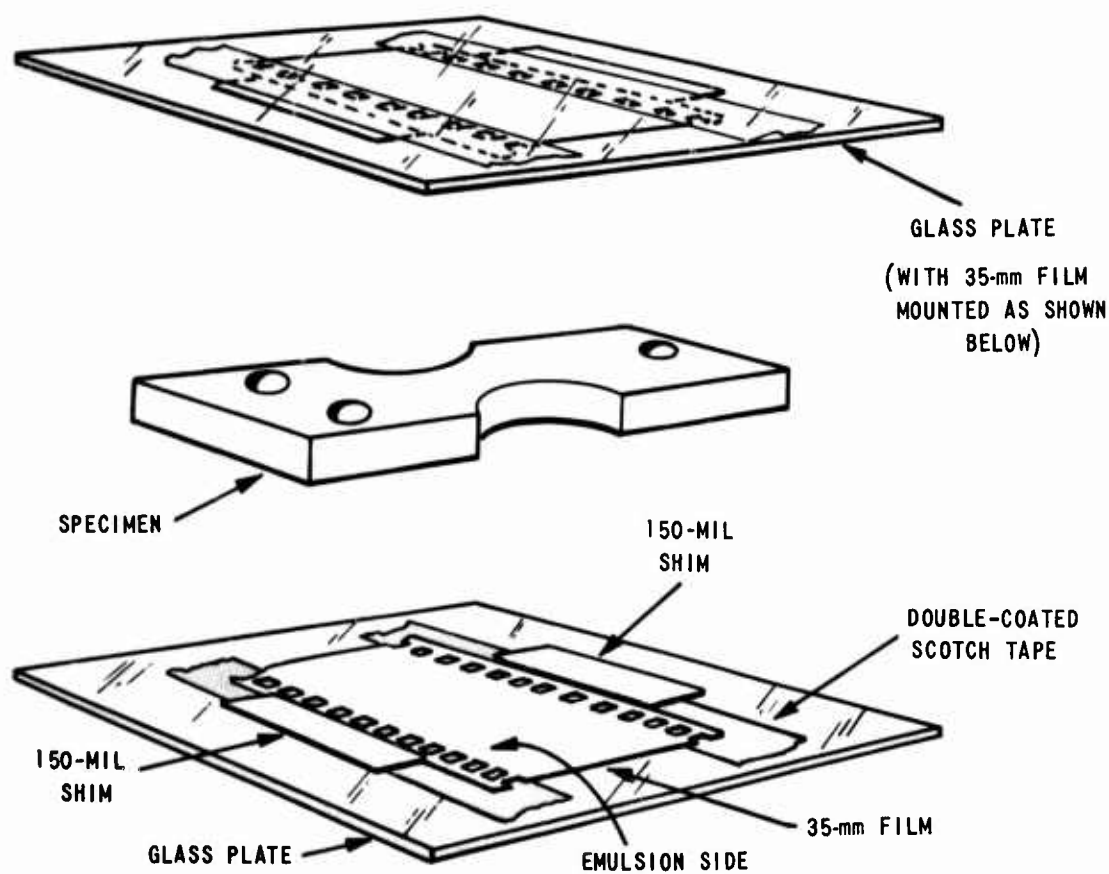
Figure 5.   RUSSELL-EFFECT TEST CONFIGURATION.
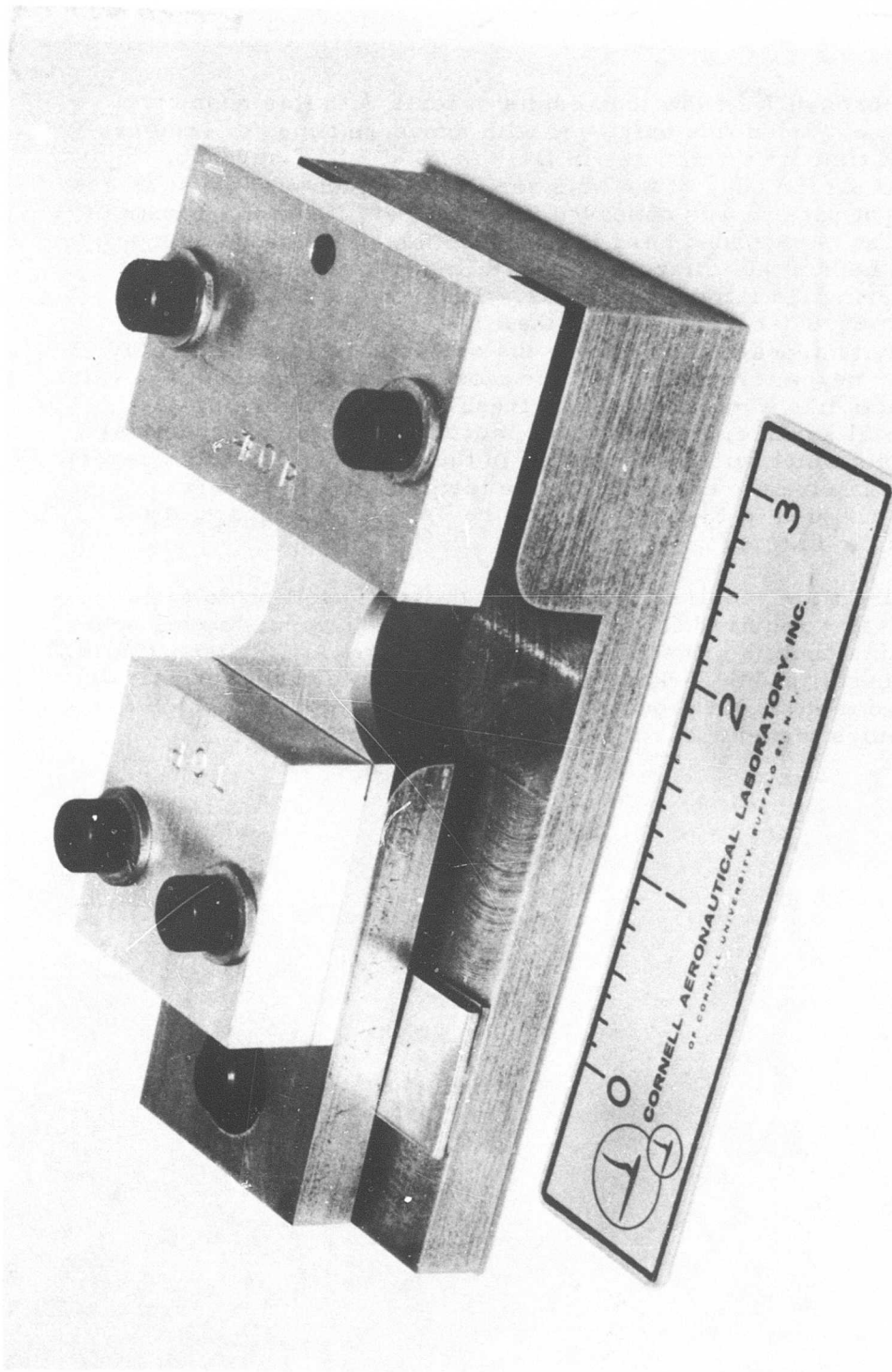
Figure 6. STATIC BENDING FIXTURE.

Figures 7a through 7d show the results of tests with this geometry.
103 a-O-type emulsion was employed with exposure times of 18 hours.
Development time was 6 minutes in D-19 at 73° F. In Figure 7b, the two
dark spots along the edge of the hole are in the region of highest stress.
A similar spot pattern was observed in other tests. One must bear in
mind that what is recorded here is an aftereffect, recorded over a
period of 18 hours; this aftereffect may differ from the initial effect
occurring during the fatiguing process. These spots are no longer
noticeable at 66,000 cycles; around the edge, however, fresh or new
sites of activity appear further along the specimen surface, possibly at
places where new microcracks and the most recent fatigue damage exist.
Similar effects,like a moving wave of fresh damage traversing the
fatiguing metal surface, became much more evident during chemical
indicator tests,which will be discussed in the next section of this report.
Upon fatigue failure,the effect due to the terminal crack is very
pronounced (as seen in Figure 7d). Figure 7e is a photograph of the
specimen in the fixture.

Because of the time required to carry out these Russell photo tests
compared to that required for indicator tests which were showing some
success at this time,the Russell photo work was gradually discontinued.
While the Russell photo work did not point the way toward a practically
useful fatigue test, it did prove the validity of the theory on which the
other indicators tested under the program are based.
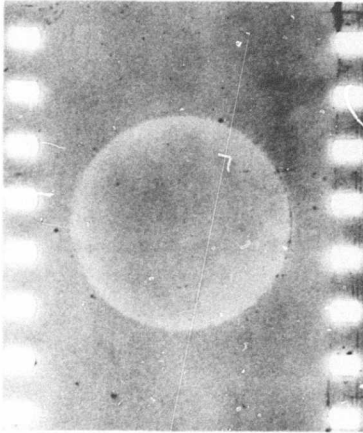
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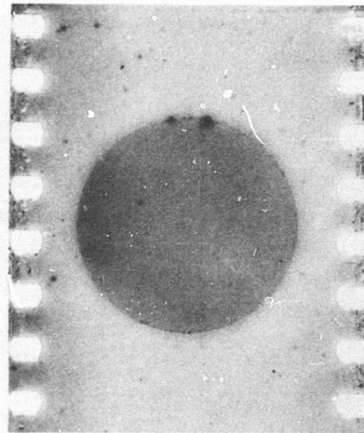
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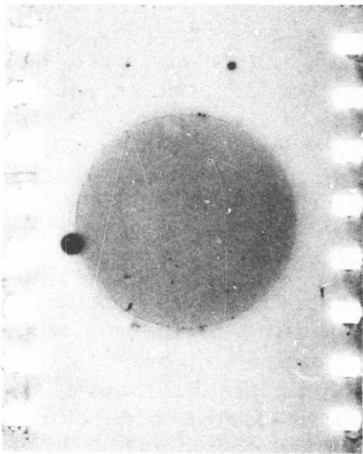
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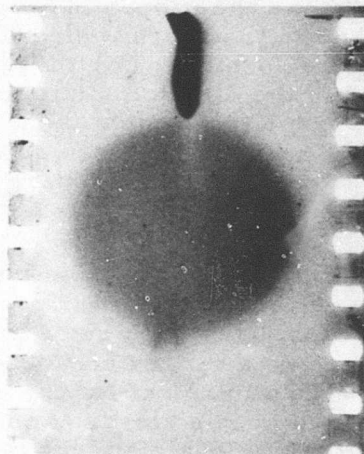
d. 103,000 CYCLES
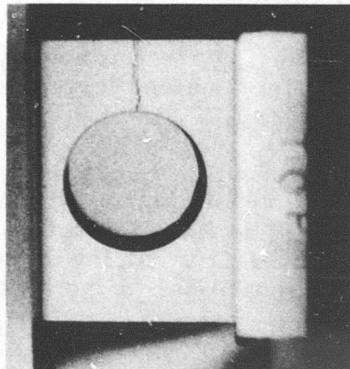
e. SPECIMEN SHOWING ACTUAL
CRACK (103,000 CYCLES)

Figure 7.   RUSSELL-EFFECT PHOTOS.

CHEMICAL INDICATORS

In addition to its role as a sensitizer of photographic emulsion, H_2O_2 was also believed to have potential as a chemical indicator. Hence, an extensive search of the literature was made to find H_2O_2-sensitive indicating agents. Candidate indicator substances were selected on the basis of the following requirements:

Sensitivity (detection of one part per 20,000 of H_2O_2 or better)

Minimum reactivity with aluminum

Distinguishable indication in the presence of H_2O_2 (color change or some other visible effect)

In many cases the properties of the indicating substances were not well enough known to assess their effectiveness, and many screening tests had to be performed. For these tests, candidate materials were prepared in the form of solutions, pastes, dry powder, and treated paper in order to evaluate them in their most sensitive form. Tests were made by noting indicator response to concentrated H_2O_2 (30%) as well as to successively more dilute solutions to determine lower limits of sensitivity.

Many candidate materials did not meet our requirements in spite of efforts to eliminate their unacceptable characteristics. For instance, several candidates required extreme acid or alkaline conditions, and, when neutralized, either became too insensitive or ceased to work at all. Mixtures containing potassium ferricyanide, phenolphthalin, and titanium sulphate are in this class. Another group of indicator candidates consisting of the sulphate and dioxide of lead, the oxide of trivalent nickel, the chloride of gold, and the oxide of silver are either oxidized or reduced by H_2O_2 to compounds of a higher state of oxidation or to free metal. This group had marginal indication capability in screening tests, and, when used on a specimen, the color change could not be distinguished. Several aniline dyes, as well as indigo and litmus, were tried with no success. The alkaloids such as quinine and nicotine, which were said to be affected by H_2O_2, showed no significant sensitivity.

Two promising indicators were developed in this screening effort. The first was a luminol-hemin-K_2CO_3 mixture in gelatin; the second was a guaiacum-diastase mixture in gelatin. The first mixture exhibits a chemiluminescent glow when exposed to H_2O_2. At low concentrations of H_2O_2 the intensity of the glow is proportional to the amount of H_2O_2 present. The mixture is made as follows (16):

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0. 1 gram of luminol (3-aminophthalhydrazide)*

2 milligrams of hemin

dissolved in 100 milliliters of a 20% potassium carbonate solution.

To coat our aluminum specimens, this solution was mixed with an equal amount, by volume, of a gelatin solution (3% by weight in H_2O). This indicator mixture was effective only when alkaline (pH of 11); it did react with fresh aluminum, which is exposed when a crack occurs in the natural or anodized oxide layer. More will be said about this later in this report.

The second mixture, which turns from amber to a dark blue violet in the presence of H_2O_2, is compounded as follows:

40% by volume	Tincture of guaiacum	(10% guaiacum by weight in ethanol)
40%	Diastase solution	
20%	Gelatin solution	(10% gelatin by weight in water)

The diastase solution used in this indicator was basically as recommended by Schöne (17), consisting of the stock solution:

Diastase	500 gram
Water	350 gram
Glycerin	700 gram

diluted 1:24 with water and filtered to provide the working solution. This mixture was slightly acidic, with a pH of 5. 5; it did not react with the specimen metal in any significant manner until fresh metal was exposed.

In summary, all the chemical indicator candidates uncovered by an extensive search of the literature and by inquiries made with industrial chemical concerns were investigated thoroughly. Further search and test effort would, in all likelihood, have a low probability of success.

GUAIACUM-DIASTASE GELATIN

The guaiacum-diastase-gelatin indicator mixture was compounded so as to achieve optimum sensitivity. However, it requires several minutes to respond fully to H_2O_2 by a color change from amber to dark blue violet. Two specimens were fatigue-tested with this indicator. One specimen had an anodized oxide coating 1000 Å thick; the other was etched but unanodized.

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* Sold by Eastman under the name 5-Amino-2, 3-dihydro-1, 4-phthalazinedione

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The results were interesting in that dark-blue spots developed in isolated fashion over the surface, developing first in the regions of highest stress concentration. The spot pattern in its early stages resembled very closely the spot development observed in our Russell-effect photos, though more spots developed. Also, the spots continue to grow or form and are permanent because this indicator is irreversible. Later in the specimen fatigue-life span, fine crack-like stain lines appeared to form at many of these spots. Bubble formation accompanying the color change was evidence of weak chemical reaction with the indicator, which is mildly acidic (pH 5.5).

The guaiacum-diastase indicator had the drawback of considerably shortening specimen fatigue life at the high stress level(by a factor of $\approx 30\%$). Glycerin is the ingredient probably responsible for this life shortening. It is not known whether the glycerin alone reacts chemically with the metal or whether it only allows the reactive indicator to penetrate cracks more effectively by lowering the surface tension of the indicator. When glycerin was used as an additive to prevent drying of the luminol indicator, a similar decrease in fatigue life occurred. According to Schöne (17), glycerin is required as a preservative for the diastase. It may be possible to develop a guaiacum-diastase formulation that does not have this adverse effect on specimen life, but time and monetary constraints precluded such effort.

LUMINOL-HEMIN GELATIN

Fatigue tests were made with 2024-T3 aluminum alloy specimens coated with the luminol-gelatin indicator.

These coatings were applied warm,and thickened or partially dried about one minute after application. Warming was needed to ungel the mixture for coating with a brush. An attempt was made to increase the wetting power of the indicator and also to retard drying by adding glycerin. A 12% glycerin content retarded drying appreciably; however, a considerable reduction in specimen fatigue life occurred. This reduction amounted to an average of about 25% for the four tests made with the two etched and two unetched specimens. Considerable reaction bubbling on the surface and the specimen weakening led to abandonment of the glycerin additive, though the cause of the detrimental effect is not apparent.

These tests were performed in an air-conditioned darkroom, where a temperature of 73° F and a relative humidity of 75% prevailed on the average. Chemiluminescence was observed with the dark-adapted eye when the specimens reached approximately 1/3 of their fatigue life in the case of specimens with a thick oxide layer (in these cases, 1000 Å to 2000 Å). In these tests the glow appeared to have a maximum in the middle third of the specimen's fatigue life.

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Typically, when from one-third to two-thirds of the fatigue life is reached, irregular, dark crack-like stain lines begin to appear at the indicator aluminum oxide interface in the curved area of the specimen, where the stress concentration is highest. These irregular stain lines grow with further fatiguing to form networks which spread toward the center of the specimen from both curved edges. These networks are joined at the time of failure. The final (failure) crack usually follows the most intense portion of the line network quite well. This visible indication of supposed microcrack growth occurs well in advance of any visual crack indication that one could normally observe on a specimen with the unaided eye. Ordinarily, fatigue cracks are not visible until about 80% to 90% or more of the fatigue life has been reached. Although mild chemical activity is evident along the stain lines, no significant shortening of fatigue life due to this effect was observable in tests to complete failure.

In case of anodized specimens, chemiluminescence occurred before the stain lines formed but diminished as the stain-line network developed. In contrast, an etched but unanodized specimen, tested under the same conditions with the luminol-gel indicator coating, yielded no chemiluminescence detectable by the dark-adapted eye, even though the crack-like stain lines developed.

Fatigue tests with indicator-coated, unetched-unanodized specimens also displayed a chemiluminescent glow and the appearance of a crack-like stain network. In such cases the glow often appeared sooner, perhaps at 10% of the fatigue life.

These effects due to the luminol-hemin-gelatin indicator were studied in greater detail in the several test series which followed. In all, 67 specimens were tested. The various effects showed considerable complexities, as will be reported in more detail in the next sections.

Chemiluminescent Glow

A photometer was employed to measure and record evidence of glow by luminol after efforts to record the glow by photography failed because the photographic emulsion was not sensitive enough.[*] In order to obtain useful records over the required range, photometer sensitivity was increased by a factor of six by removing a UV-absorbing filter. A recorder monitored the photometer output and provided a time history of glow intensity. The 3/8-in.-diameter field of view of the instrument was aligned on the specimen so as to include its top surface and a portion of the edge where the glow appeared most intense to the eye.

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[*] The use of an image intensifier is recommended for any further effort to record the glow by photography.

This work was performed in conjunction with the color indication tests, since the same chemical served as indicator for both. The photometer recorder was used to explore evidence of correlation between glow initiation and stain indication. However, since such correlation was not readily evident and the glow, though recordable in total darkness, was too weak to be practically useful, project effort on photometric measurements was halted.

However, a limited study under internal (CAL) sponsorship was initiated in order to explore questions of scientific interest: the dependence of glow onset and intensity on the thickness of the oxide coat; the dependence of glow onset on stress level; further effort to discover the relation, if any, between glow and staining; and, finally, some exploration of variables, not necessarily fatigue-related, that influence glow and stain phenomena. This internally sponsored work is reported in the Appendix.

Crack Staining

The crack-like staining which was described in the previous section was studied in considerable detail. Chemical reactivity between the luminol-hemin-gelatin indicator coating and freshly exposed aluminum was not considered detrimental to our project goals, since this reaction resulted in visible crack-like stains in those areas where fatigue cracks could be expected to develop, and the fatigue life of the specimen was not shortened.

Photographs were taken at appropriate intervals during fatigue tests with luminol-gel-coated specimens. Figure 8 shows the development of such a crack network on a specimen with a central hole. Specimens of this geometry have a nominal fatigue life under our load conditions of $103,000 \pm 6,000$ cycles.

Evidence that the crack-like stains coincide with actual fatigue micro-cracks was obtained from studies of several fractured specimens with an optical metallurgical microscope. For instance, isolated crack-like stains on indicator-coated specimens greatly resemble the isolated microcracks found on uncoated specimens. Also, cracks have been observed within the stain lines. Such cracks are about one-fifth the width of the stain.

The question as to which ingredient in our luminol-gelatin indicator is responsible for crack staining was answered in one simple test. An etched specimen was coated around one edge with a potassium-carbonate-gelatin mixture of the same proportions as contained in our indicator, and the other edge with a correspondingly proportioned mixture of gelatin and water. Light crack staining occurred at the usual test time on the side whose coating contained K_2CO_3 and not on the side containing pure gelatin. We concluded that the alkaline K_2CO_3 is responsible for the crack-staining
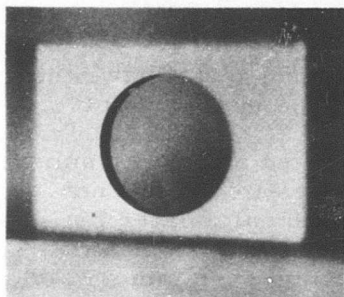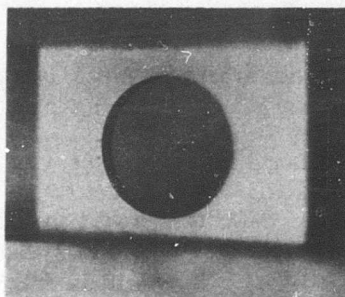
a. 62,000 CYCLES   b. 64,000 CYCLES   c. 72,000 CYCLES
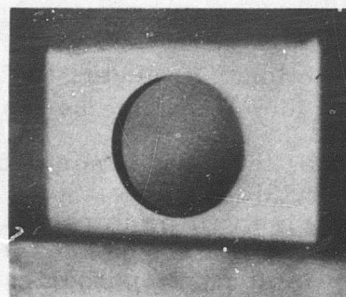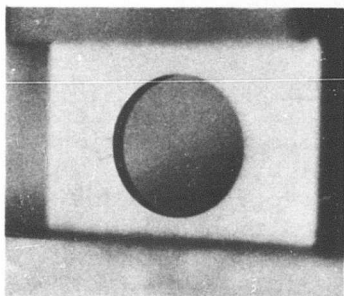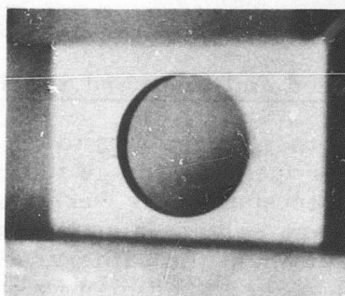
d. 78,000 CYCLES   e. 88,000 CYCLES   f. 91,000 CYCLES
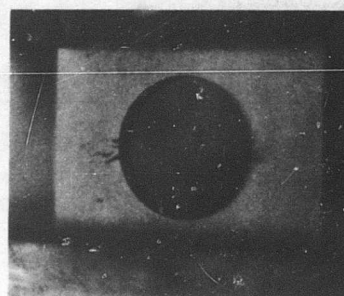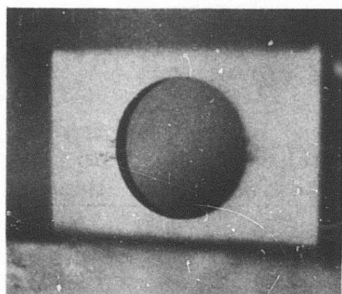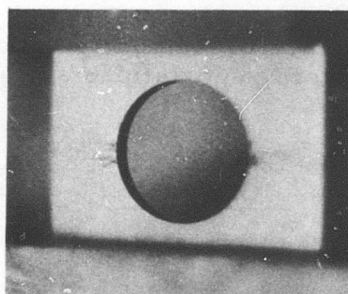
g. 98,000 CYCLES   h. 108,000 CYCLES   i. 108,000 CYCLES
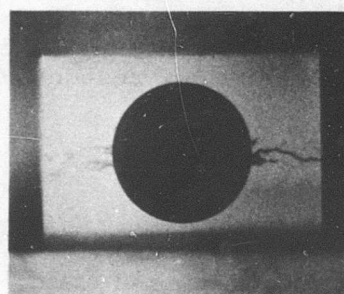
Figure 8.   STAIN MARKS (LUMINOL INDICATOR).

reaction. However, the darker staining usually found suggests that either the luminol or the hemin or both are responsible for the deeper color.

In all the tests described so far the indicator was applied at the beginning of cyclic loading. Since the ability to discover damage after component service will be important, the effect of applying the indicator later in the fatigue life of the specimen was tested for an etched and an unetched specimen. In neither case did crack staining develop on specimens which stood unloaded for 15 minutes after 60,000 cycles of stress application. When flexing was resumed, the stain marks began to form on the etched specimen after only 1,500 additional cycles. From these observations, we concluded that the indicator functions only when fresh surface is exposed.

Staining Effects on Etched and Unetched Specimens

The purpose of another test series was to determine whether prior etching is preferable for fatigue-damage indication by crack staining. Ten unanodized specimens were tested; four specimens were etched, and six were solvent-cleaned only. Although the crack stains appeared at about the same time during the test cycle, the stain pattern on the etched specimen was much clearer with finer details and somewhat less reaction (bubbling). Further, in the unetched case there was difficulty in getting the indicator solution to wet the surface. We concluded that etched specimens should be used in all further tests.

The results of the tests are presented below in averaged form with their respective average deviations about the mean:

	Etched and Coated	Unetched and Coated	Unetched and Uncoated
Number of cycles to beginning of stain	25,000 - 30,000	30,000 - 35,000	-
Number of cycles to failure	111,000 ± 10,000	107,000 ± 6,000	97,000 ± 2,000
Total Combined Average	109,000 ± 7,000		

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It will be noted that the fatigue life of the uncoated specimens had the smallest average deviation about the mean. This smaller spread is ascribed to the fact that these tests ran without interruption, whereas all other tests in this series were interrupted at intervals for crack stain photography.

Crack Initiation

To study the effects of the luminol indicator on the initial formation of cracks a series of ten tests was run at the high stress level ($\approx 35,000$ psi, 100,000-cycle life). This was done to determine whether the indicator solution could bring about crack formation through such mechanism. as stress-corrosion cracking, which would account for the fairly intricate stain pattern and, especially, the associated crack network which we did not observe with uncoated samples.

Indicator was applied to one-half of the top face of each specimen just prior to fatiguing. The half chosen for coating was alternated from one test to another. All ten samples were then fatigued to 40,000 cycles, electropolished, and observed under the optical microscope,with the result, in every case, that evidence of cracking was significantly more pronounced on the coated half --there were more cracks and they were longer (see Figure 9). An additional specimen was fatigued to 30,000 cycles, and no damage was observed on the uncoated half although a number of fairly long (one millimeter or more) cracks appeared on the coated half.

We concluded from this test series and from the results tabulated on the preceding page that interaction between indicator and specimen enhances crack initiation but, in spite of that, extends specimen time-to-failure. This extension of time-to-failure was also found in the 500,000-cycle tests which followed.

500,000-Cycle Fatigue Tests

In two initial 500,000-cycle tests, the indicator was applied every 100,000 cycles and removed 40,000 cycles thereafter, following visual observation and photographic recording of surface condition. Results were inconclusive, apparently because the amount of indicator, reaction products, and water remaining on the specimen could not be controlled.

Another group of tests was then conducted in which the indicator was applied only once to each specimen and left there until fatigue failure. This practice was found to be an improvement over the one described above insofar as control is concerned. The results of these tests point toward a longer lifetime for specimens coated with indicator which has had time to dry.

25

0.004"

UNCOATED SIDE   COATED SIDE
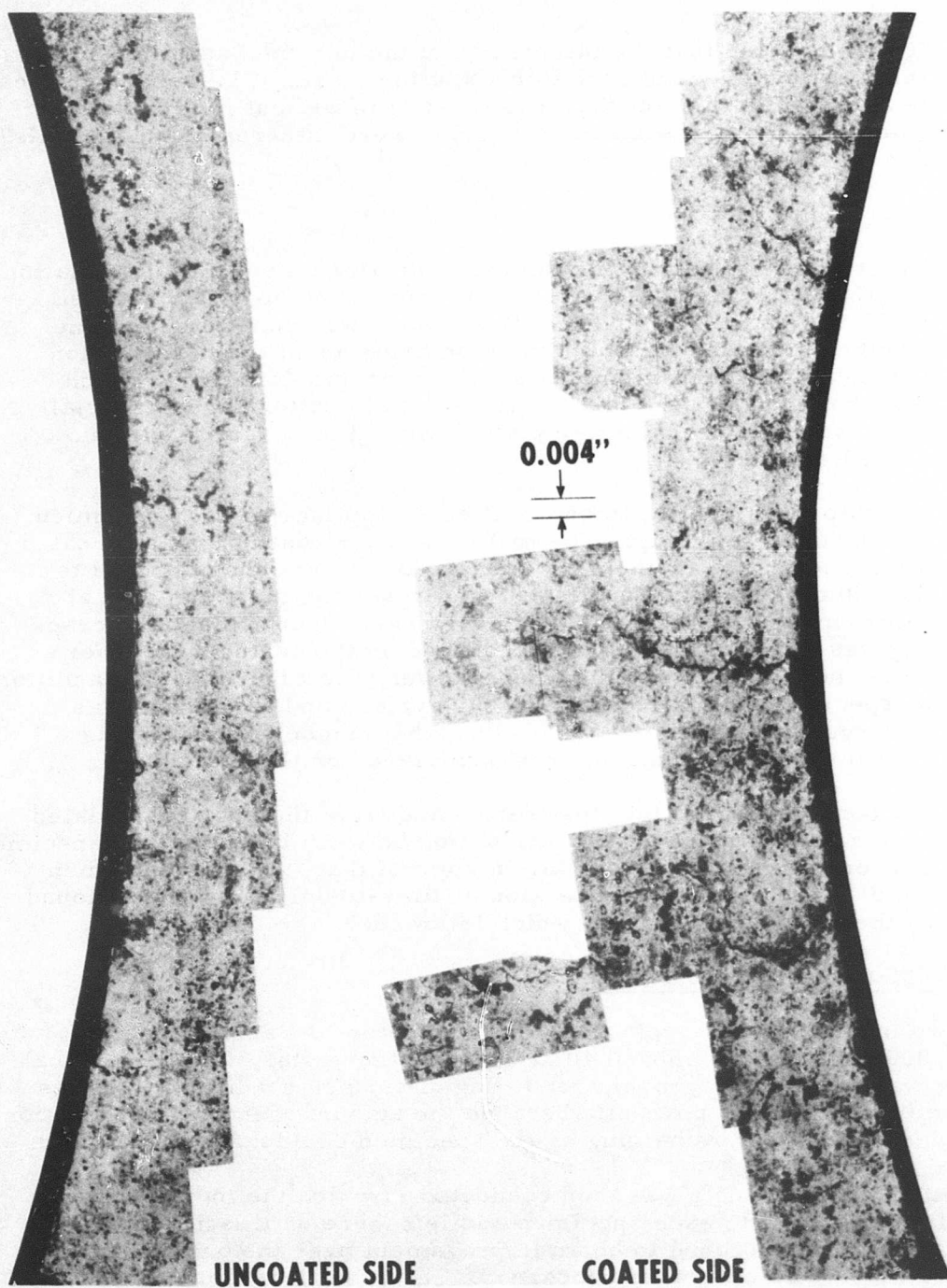
Figure 9.   COMPARISON OF CRACK FORMATION (40,000 CYCLES).

Crack stains found in this group of specimens appeared as a few short lines (typically 1/10 in. or less in length), in contrast with the more complex network of stains found on specimens tested at the higher (± 35,000 psi) stress level.

The results of the first nine tests are tabulated below:

Application of Indicator at: (thousands of cycles)	Failure at: (thousands of cycles)
400	523
300	617
300	374
200	492
100	435
none	393
"	338
"	415
"	455

Additional fatigue tests in the 500,000-cycle-life range were made with luminol-type indicator coatings applied at the start of tests. Efforts were made to prevent the indicator from drying out during the fatigue life of the specimen. A plastic canopy around the specimen and holding clamps were tried as well as the addition of more indicator and water. In both cases, crack stain lines developed, but no network resulted. Also, the lines developed quite slowly and extended over only a fraction of the surface before failure.

It became apparent that no matter how the indicator was applied, or in what condition it was maintained during these low-stress fatigue tests, the crack network did not develop as it did in the high stress tests. Results of the replication studies reported on page 31 indicate that crack development in the low-stress case is indeed different.

The following conclusions were drawn from the long-life tests:

1. At low stress (500,000-cycle life), there was found to be far less staining than had earlier been observed in high-stress tests (100,000-cycle life). This comment pertains to equal times of contact of moist indicator with the specimen surface.

2. The observed strengthening influences of the indicator may be dependent upon the time within the specimen's fatigue life at which indicator is applied. In contrast, since application of indicator requires that specimen flexure be stopped,

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there may be some relaxation of the fatiguing process during the rest periods whereby specimen lifetime is prolonged.

1,500,000-Cycle Fatigue Tests

Fatigue tests on a few specimens were made at the 24,000-psi level ($\approx 1,500,000$-cycle life) in order to determine the nominal fatigue life and the experimental variation limits. However, no tests were made with indicator coatings at this stress level due to shortage of funds. There was considerable variation in specimen life, but failure characteristics were similar to those for the higher stress cases; namely, the breaks were abrupt; cracks were not visible until the last few thousand cycles before break.

PHOSPHOR TESTS

The phosphor method of detecting exo-electron activity was considered as a means of utilizing emitted electrons directly. The principle here is that the exo-electrons would excite the phosphor to emit light in those areas where they originate. This method requires that the electrons obtain an energy at least equal to the excitation energy of the phosphor. As the emission energy of most of the exo-electrons is likely to be low, less than one ev, only those phosphors with the lowest obtainable activation energies are likely to work.

We selected the hex-ZnO:Zn (zinc-doped zinc oxide) reported by Schrader and Kaisel.(18) They reported on excited luminescence in ZnO:Zn with electrons of energy less than that of the emitted photons; according to the interpretation given (18, 19), the electron assumes the internal potential of the phosphor crystal lattice upon entering it. For hex-ZnO:Zn in vacuum,the internal potential is higher than the excitation energy for luminescence. In order to achieve this type of low electron-energy excitation,it is essential that charge buildup on the thin phosphor layer be prevented. Since it is somewhat electrically conductive, ZnO:Zn can achieve this condition when placed on a conductive substrate. In our case we would not be working in a vacuum. Therefore, it was essential to have intimate contact between the phosphor and the electron-emitting metal oxide so that the electrons could enter the phosphor. Thus, the phosphor had to be coated with a semitransparent conducting film.

A sample of hex-ZnO:Zn was provided by R. E. Schrader, the author of Ref. 18, at RCA Princeton Lab. This material is normally deposited on a surface by allowing it to settle out from an alcohol suspension. Since no binders can be used (purity of the phosphor is essential),the deposit is very fragile and would flake off from our vibrating specimens quickly. It was decided that the phosphor would be deposited on the specimen in a vacuum by evaporation. Such a coating would adhere well and give optimum contact between phosphor and metal oxide surface. A vendor with past experience with ZnO deposition work was given the task. ZnO deposition presents a problem because the oxide undergoes partial decomposition when heated to the necessary evaporation temperature in a vacuum. Consequently, one obtains a deposit on the specimen which is excessively rich in zinc and which must be reoxidized by baking at an elevated temperature in air. However, this treatment will weaken the aluminum alloy if not carried out properly. By heating the coated specimen to 900° F for 15 minutes and cooling quickly with cold nitrogen,the excess zinc was oxidized,and the aluminum was left in the T4 heat treatment condition. In this condition it had nearly the same fatigue strength as in its original T3 condition. The resulting specimen was given a thin, conducting, but partially transparent, overlayer of chromium metal by

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vacuum evaporation.   The specimen was tested at 35, 000 psi and failed after 135, 000 cycles.   In complete darkness, no glow was seen by two observers whose eyes remained dark-adapted throughout the test.

It became evident from our experience with this exploratory test that considerable effort would have to be expended to fully investigate phosphor-type fatigue indicators. We do not recommend further pursuit of such indicators, especially where field or depot-operational requirements must be satisfied.

REPLICATION AND MICROSCOPY

Replication of the specimen surface and microscopic observation of these replicas was planned as an independent-control means of assessing surface fatigue damage. The method is nondestructive and provides a faithful reproduction of surface features which can be studied with either an optical or an electron microscope. The principal surface features produced during cyclic fatigue are slip bands and microcracks. Observation of slip bands is possible only at magnifications obtainable by electron microscopy and was not pursued, because it is time-consuming and because useful information was much more readily obtainable by optical microscopy. Microcrack formation and propagation were observed in our study as the most convenient and practical surface effect observable with an optical microscope.

Preliminary tests were conducted to establish:

1. best time to replicate for crack correlation studies

2. best condition of the surface to reveal the cracks

Replicas of the machined and etched surface of one flexure specimen were made every 10,000 cycles starting at 20,000 cycles and continuing up to specimen failure at $\approx$ 100,000 cycles.

These replicas were made by applying acetone-softened cellulose acetate tape under pressure to the surface of the specimen during a short interruption of the test. After the acetone evaporated, the replica was removed from the specimen and roto-shadowed in vacuum with germanium at an angle of 30°. A carbon film was deposited on the germanium in order to provide support for the second replica in the event electron microscopy was necessary. All investigations of these replicas reported here were performed with an optical microscope at a magnification of 170X.

Cracks were first found on a replica taken after 40,000 cycles of flexure. Surface roughness due to the chemical etch made crack observations difficult; roughness was severe enough to obscure the true extent of cracks. Subsequent electropolishing of the failed specimen produced a surface that was fine-grained enough to determine that crack length was substantially greater than that shown in the etched-only surface. Ideally, the specimen surface would have to be electropolished at the start of the test. As mentioned previously, our attempts to electropolish specimens prior to fatigue tests early in the program were unsatisfactory. However, results satisfactory for the purpose of these replication studies were later obtained by first etching and then electropolishing only the central (high-stress) area of the specimen. Two specimens were prepared in this manner. One was fatigue-

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tested at the high stress level (35,000 psi) and replicated every 10,000 cycles, starting at 10,000 cycles and continuing to failure. The other was fatigued at an intermediate stress level, 27,000 psi, and replicated approximately every 50,000 cycles, starting at 100,000 cycles and continuing to failure (307,000 cycles).

Since specific surface details could not be followed without considerable effort, it was decided to monitor the crack growth in specific regions of the specimen. These regions are defined in Figure 10.

Two photographs of each region were made. The first photograph was made in bright field-reflected light, and the second photograph of the same region was made in polarized light. This technique allows for the positive identification of a crack. For an apparent crack to be counted in the crack length measurements, it must appear on both photographs. Crack lengths were photographed at a magnification of 254X, and measurements were made from the photographs with an accuracy of approximately 10%.

Average crack length was computed by treating all of the five areas with equal statistical weight. This technique is convenient and valid throughout most of the fatigue life. However, some ambiguity results near the end of fatigue life, since growth of the failure or terminal crack is greater than crack growth in the surrounding regions. Actually this average crack length measurement technique is based on the assumption that the failure crack is not included in the data. One would expect the average length for all cracks to increase during fatigue until a failure crack became well formed and began to grow rapidly. At this stage, near the end of fatigue life, all other cracks would exhibit little or no growth in length, and the assumption can be made that they also would cease to grow in depth. No observations on change in crack depth are available in support of this assumption, however. Average crack length growth measurements for these two specimens tend to confirm this model of crack development. For the 35,000-psi stressed specimen, no further crack growth occurred after 80% of fatigue life. For the intermediate stressed specimen, this point was reached at about 80% of fatigue life.

A brief summary of the results of the aforementioned crack study for the two specimens is given below:

1. For the high-stress case (35,000 psi), crack growth rate and length were greatest at the center of the specimen, near the edge.

2. For the low-stress case (27,000 psi), crack growth rate and length were greatest near the center of the specimen.

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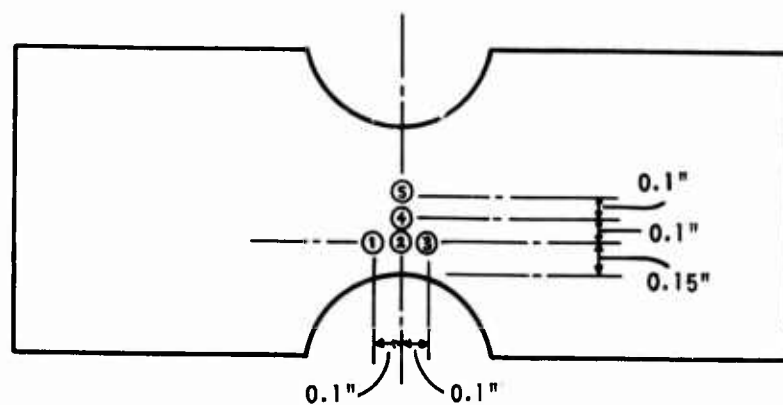
Figure 10.   REGIONS FROM WHICH CRACK GROWTH MEASUREMENTS WERE MADE.

3. Crack growth rate was approximately linear for the high-stress case up to 80,000 cycles. The crack growth rate was 10 μ/1000 cycles.

4. Crack growth rate was approximately linear for the intermediate-stress case up to 250,000 cycles. Up to this time there was an average growth rate of 1 μ/1000 cycles.

5. Crack length became constant after 80% of fatigue life for both the high-stress case and the intermediate-stress case.

Results (1) and (2) are in qualitative agreement with the luminol-gel-coated specimen crack stain results.

CONCLUSIONS AND RECOMMENDATIONS

1. The Russell effect appears to be impractical for depot or field application as a fatigue indicator because the process requires darkness, controlled humidity, and inconveniently long exposure time. The method does indicate the presence of H_2O_2-active sites on fatigued aluminum, i.e., sites of presumed exposure of fresh base metal that are related to fatigue failure.

2. Cuaiacum-diastase gelatin, a color-change indicator, which turns a dark blue-violet in the presence of H_2O_2, gives a permanent record of the positions of individual H_2O_2-active sites. As compounded and used in our experiments this indicator appeared to cause a reduction in fatigue life of 2024-T3 aluminum test specimens. We feel that this undesirable side effect may be eliminated by changes in compounding. Because of its ease of application and positive form of indication, we recommend its further development. At this point, the relation between indicator reaction and lifetime-to-failure is not predictable.

3. Luminol-hemin gelatin, a chemiluminescent indicator, yields a measurable glow in the presence of H_2O_2. The chemistry of its reaction is complex and the glow produced depends on more factors than the amount of H_2O_2 present. Because observations of the chemiluminescent glow must be made in the dark, it is not recommended for field or depot use.

   "Crack staining" associated with the use of this indicator did not depend on H_2O_2 production but on some other activity more akin to chemical stress corrosion. At high stress the staining showed potential as a fatigue-damage indicator; at low stress the effect was less prominent. Since this effect occurred only under dynamic stressing, and not under quiescent conditions, we do not recommend further development work.

4. Early fatigue damage, before cracks appear, is observable at high magnification by surface replication and electron microscopy. Low magnification (light microscopy) reveals fatigue cracks under quiescent conditions following stress. On the basis of our present limited study we feel this technique has capabilities for determining the fatigue condition of a material or part. Replication studies at low magnification would be particularly useful at stresses

leading to short fatigue life, where, in the alloy tested by
us, surface cracks are numerous and readily detectable.
We recommend further development of this method.

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APPENDIX[*]
SURFACE-CHEMICAL REACTIONS IN A
METAL UNDERGOING FAILURE

This appendix is specifically concerned with mechanisms controlling the chemiluminescence of certain organic materials in contact with surfaces of metallic materials undergoing cyclic stress to the point of failure.

Motivation for this study came from certain observations during pursuit of Project TRIFFID. There, the objective was to find an "indicator" responsive to the progress of fatigue effects in a stressed material, that response hopefully being translatable into a value of lifetime remaining-to-failure. That objective was not fully realized, nor were program requirements such as to permit detailed consideration of basic mechanisms involved. It is for the latter reason, in particular, that this supplementary study was undertaken.

The following three statements constitute the framework on which this study hangs:

1. There is ample evidence[**] that when <u>fresh</u> metal surface is exposed jointly to moisture and oxygen, the formation of H_2O_2 results.

2. There is evidence that H_2O_2 is an important - perhaps even a necessary - ingredient in the stimulation of chemiluminescence from the organic material luminol ($NH_2C_6H_3CONHNHCO$).[***] The brightness of such luminescence is considerably enhanced by the presence of certain metal-organic complexes which act either as activators or catalysts, depending upon the chemical environment.

3. Chemiluminescence is observed in a luminol solution ("fortified" by a metal-organic compound) applied to the surface of 2024-T3 aluminum alloy specimens undergoing cyclic stress.

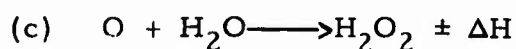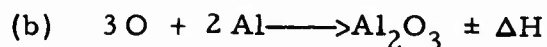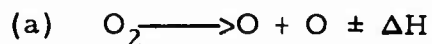# FORMATION OF H_2O_2 AT DISTURBED METAL SURFACES

In the several references listed (4, 13, 20-27), the authors examine the consequence of exposing "clean" metal surface to an environment containing both moisture and oxygen. Without exception they either observe or admit the presence of hydrogen peroxide. Many of the authors refer to a paper by Russell (4), who seems first to have called attention to H_2O_2 formation at an abraded surface.

While the several experimental environments do have moisture and oxygen as common ingredients, they differ in other ways, particularly with respect to the physical manner in which "fresh" surface was exposed. Roikh and his co-workers (Refs. 20-24) were interested in the atmospheric corrosion of such metals as aluminum, zinc, and magnesium. Their preparation of "clean" surfaces seems to have been somewhat casual, but each of their cited papers gives evidence of the formation of H_2O_2 from freshly abraded surfaces. In Ref. 24 Roikh and Bolotich indicate that the ratios of H_2O_2 to Al_2O_3 and H_2O_2 to MgO formed were 1:11.5 and 1:27.5, respectively, on a molar basis. They attribute the absence of a 1:1 ratio to dissociation of H_2O_2 at the surface. They say nothing of the mechanism by which H_2O_2 was formed originally.

In contrast with the methods of Roikh et al., Grunberg (17) "machined" metal specimens under water and titrated directly to measure the H_2O_2 formed. His experiments on zinc showed straightforward production of H_2O_2 in proportions relating to new surface exposed. With iron at the test material, more complicated - and less readily explainable - reactions set in, and a direct relationship with surface exposure could not be stated. Presumably, the finely divided iron Grunberg produced caused dissociation of some of the H_2O_2 that might otherwise have formed.

In discussing Ref. 24 above, the simultaneous formation of H_2O_2 and metal oxide was alluded to. It is tempting, then, to hypothesize a mechanism such that both metal oxidation and H_2O_2 formation can be accounted for.

The following rudimentary reactions may be written:

(a) $\quad O_2 \longrightarrow O + O \pm \Delta H$

(b) $\quad 3O + 2Al \longrightarrow Al_2O_3 \pm \Delta H$

(c) $\quad O + H_2O \longrightarrow H_2O_2 \pm \Delta H$

If these reactions - or any like them - are indeed to take place at a fresh surface, their "energetics" must be appropriate or they will not proceed. Ahearn and Law (25) offer a mechanism, growing out of their study of H_2O_2 production at abraded surfaces of silicon and germanium crystals, which seems to be plausible. They suggest, for reaction (a) above, "the dissociative chemisorption of an oxygen molecule, the atoms of which can then combine with neighboring absorbed water molecules." They also point out that the "rates of" image formation (i.e., formation of a latent photographic image by H_2O_2 in their Russell-effect experiment) for germanium and silicon are in the ratio 1:20, and that the oxidation rate of silicon is higher than that of germanium. The observation of Roikh (24), that metal oxides and H_2O_2 do not form in equal (molar) amounts, undoubtedly is also true for the Ahearn and Law case.

It seems reasonable, then, to conclude that we have here a satisfactory mechanism for the joint formation of metal oxides and H_2O_2 upon the exposure of "clean" metal surface to a moist, oxygenated environment.

In the foregoing discussion, observations derived from experiments involving, for the most part, "abraded" surfaces were depended upon. In the experimental situation that led to this study, the mode of surface is that of cracking due to fatigue, with ultimate failure. While the same chemical mechanism may still be involved (i.e., the dissociative chemisorption of oxygen) as an initial step, it is not clear whether the geometric configuration which constitutes a crack will permit as ready access of H_2O_2 and O_2 to the new surface as to an exposed, abraded surface. Some note of possible differences will be taken later in this appendix.

THE CHEMILUMINESCENT REACTION WITH LUMINOL AS AN EXAMPLE

The chemiluminescence of luminol is a well-known phenomenon. In selecting luminol plus hemin as a candidate indicated during the TRIFFID work, we did not resort to original references but, rather, to those which discussed the behavior of luminol in a formulary sense. The formulation selected was:

> 0.1 gram of luminol
>
> 2 milligrams of hemin

dissolved in 100 milliliters of a 20% potassium carbonate solution.

To coat the aluminum specimens, this solution was mixed with an equal amount, by volume, of a gelatin solution (3% by weight in H_2O).

The principal reason for reviewing the chemical behavior of this mixture is this. Although it was selected as a reactant to H_2O_2, and while evidence of the sort given earlier suggested strongly that H_2O_2 would be generated

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when fatigue cracks appeared, no <u>direct</u> <u>measurements</u> of the presence
or quantity of H_2O_2 in the luminol-hemin solution were made during our
fatigue tests. Further, there was concern that some unanticipated
metal complex might have entered the indicator solution so as to cause
chemiluminescence without a need for H_2O_2.

This writer believes that this concern has been dissipated and offers
the following discussion of two references which deal with the part
played by organo-metal complexes in the chemiluminescence of luminol.

Weber et al (26) (abstract only available) discuss the effect of several
iron-bearing organic compounds on the oxidation of luminol by H_2O_2. One
of these iron complexes discussed is chlorohemin, an accelerator similar
to the one incorporated in our "indicator" solution. According to Ref. 26,
such iron complexes greatly accentuate the light output from luminol,
while they are themselves more or less depleted in the process. One of
the products of luminol oxidation is O_2, which may reoxidize the
accelerator, thus restoring its potency so that it acts more like a catalyst
than a reagent. Hemin apparently is more of the reagent type, being
used up in the process of helping to generate greater luminescence.
Although there were no measurements of hemin content vs. time during
fatigue experiments, there is some reason to believe that the hemin is
depleted.

Another reference, Ojima (27), also considers the chemiluminescence
of luminol in the presence of metallic (metal-organo) complexes. One
such group of materials consists of copper-amine compounds, whose
behavior is like that of the iron complexes studied by Weber. These
require the presence of H_2O_2 for the oxidation of luminol (to lead to chemi-
luminescence), and the chemical reactions outlined by Ojima and Weber
are essentially the same. The dependence of luminous output on
solution pH is also demonstrated.

Ojima, however, also describes certain reactions involving cobalt-amine
complexes (which one would expect to behave like iron complexes because
of their similarity), for which he claims no need for H_2O_2 in the solution.
While in the work conducted by CAL there could scarcely have been any
such cobalt complex present, the existence of this apparent exception
to the rule gave some pause. Interestingly enough, a more careful
analysis of Ojima's work shows that H_2O_2 is <u>formed</u> as an intermediate
in a luminol oxidation reaction that, initally, requires O_2 rather than
H_2O_2. Subsequently, the intermediate H_2O_2 breaks down to form two
OH radicals that react with an intermediate (metastable) luminol peroxide
to form an "excited" or unstable luminol-like molecule, which decays
to a final, stable state with the emission of a quantum of light energy.

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In summary of the two foregoing sections, it appears that:

1. H_2O_2 is developed, together with the formation of metal oxides, when "clean" metal surfaces are exposed to a moist-oxygen environment.

2. Where the above reaction may occur and there is luminol present, then the observation of chemiluminescence appears to provide evidence for the existence of H_2O_2.

The above two arguments are rather "circular" in character but are believed to be independently valid.

IMPLICATIONS FOR FATIGUE TESTS USING LUMINOL INDICATORS

As stated earlier, the object of Project TRIFFID was to develop a fatigue indicator that would provide information on lifetime-remaining-to-failure. Of a wide variety of stress-to-failure tests employed in this investigation, three groups are of interest here. In all of these tests, luminol-hemin indicator solution was applied just prior to the start of tests; the same stress level, ± 35,000 psi, was maintained for all tests; lifetimes-to-failure were in the range 90,000 to 130,000 cycles. These tests were run principally to determine whether surface condition had any bearing on brightness or time history of the observed chemiluminescence.

The three sets of tests involved:

1. Three specimens with no surface treatment. Natural oxide was, of course, present. Specimens 14d, 16d, and 18d were employed (curves 1, 2, and 3 of Figure 11).

2. One specimen, the surface of which was etched to remove scratches and other surface injuries. Presumably, a natural oxide coating - perhaps 25 Å thick - had grown on the specimen before fatigue testing began (curve 4 of Figure 12).

3. Seven specimens, surface-etched and then anodized to form oxides with thicknesses varying from 250 Å to 3000 Å. Specimens 11, 8, 102, 4b, 6, 13, and 101 were used (curves 5 through 11 of Figure 12).

These conclusions, some of them negative, can be drawn from Figures 11 and 12.

1. The onset of luminosity at about 10,000 cycles with unetched specimens, as compared with the 25,000- to 40,000-cycle onset for etched specimens, suggests that surface (oxide) structure was weaker, and that exposure of "clean" alloy
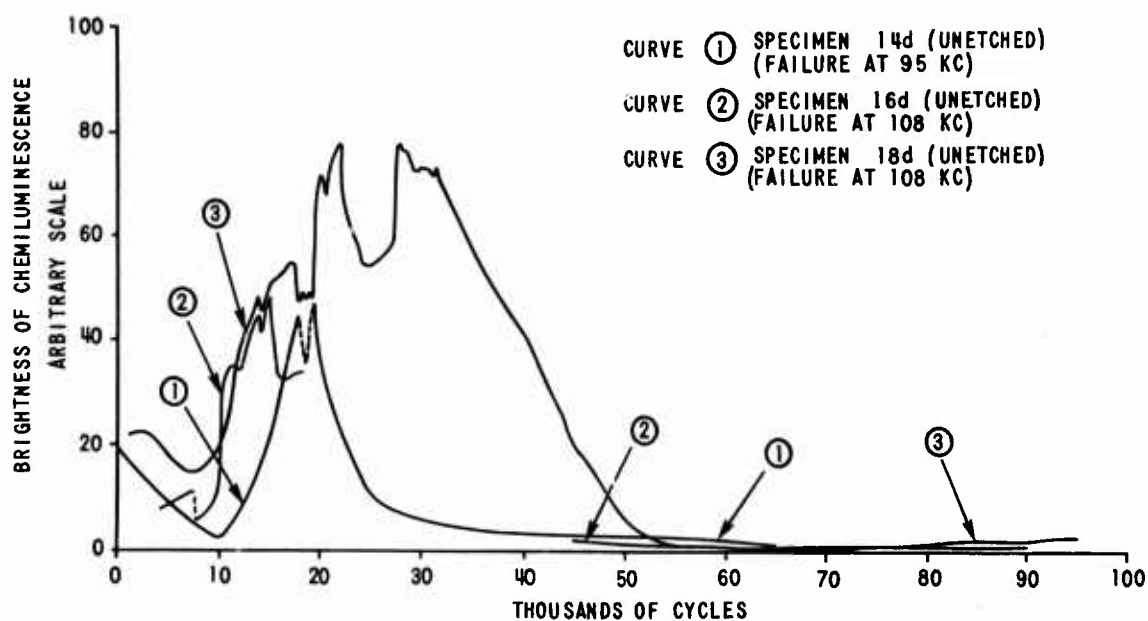
44

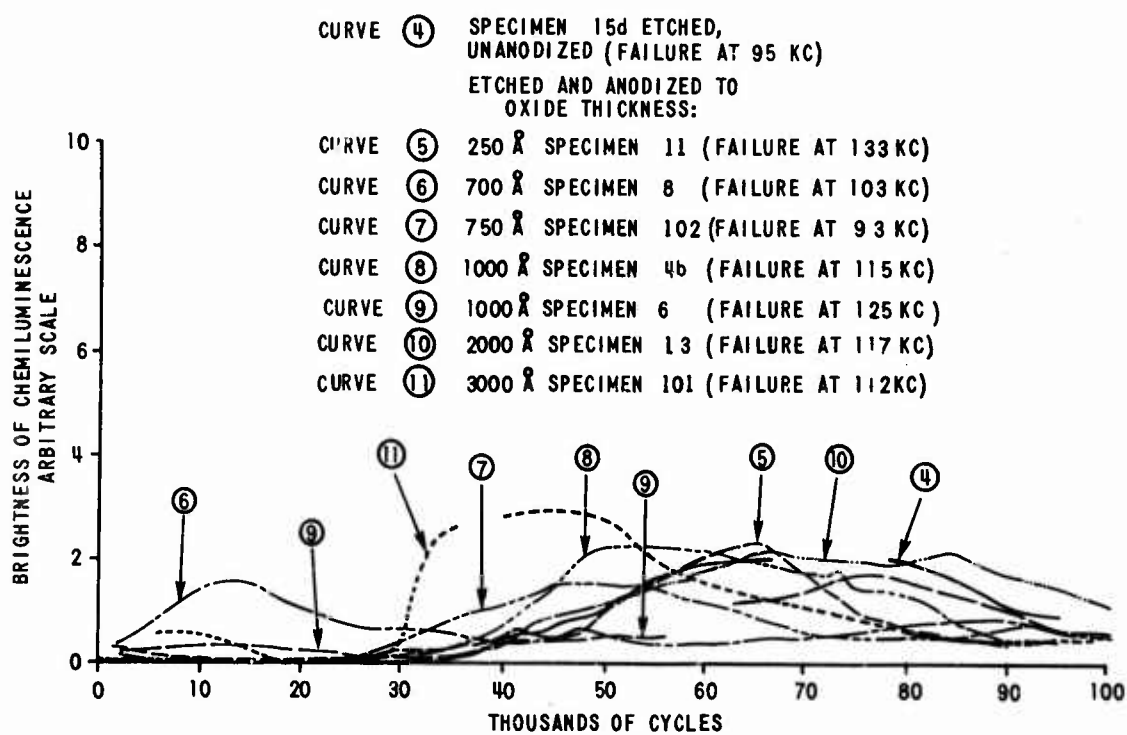Figure 11. APPROXIMATE REPRODUCTION OF PHOTOMETER TRACES.

Figure 12. APPROXIMATE REPRODUCTION OF PHOTOMETER TRACES.

through the oxide came sooner, for the unetched cases.

2. In contrast with (1), the results from specimens that were etched or etched and anodized before stressing suggest that re-formation of the surface has improved its resistance to crack initiation. The later onset of luminosity observed in curves 4 through 11, Figure 12 (exception, curve 6), is the important clue. Other tests, not reported in this appendix, indicate that surface cracks do not begin to appear (as determined by microscopic examination of specimen surfaces) until about 40,000 cycles at 35,000-psi loading (with or without indicator).

3. Observations of fatigue-crack growth, discussed in the Replication and Microscopy section of this report, indicate that crack length increases at a quasi-linear rate up to about the 80% point in fatigue life. From that point to failure, crack growth appears not to be linear.

If crack growth is linear, as seen by surface measurement, then the rate of clean-surface exposure will tend to have some time dependence at a power greater than unity, because crack depth is increasing as well. Thus, if it can be assumed that reactants can penetrate cracks to reach the clean surface, there should be a greater-than-linear rate of H_2O_2 development and, jointly, a light output from the luminol-oxidation reaction.

Figure 11 suggests that the latter argument is followed in a general sense, at least just after the onset of luminosity. In contrast, however, is the observation that luminosity does not continue to rise as cracks continue to open and/or lengthen. There are several possibilities to explain this finding:

1. Grunberg (13) and Ahearn and Law (25) indicate that as fresh surface appears, it soon is withdrawn as a participant in the H_2O_2-producing reaction because it becomes oxidized. Thus, the period during which fresh surface remains as yet unoxidized, rather than the total amount of new surface ever exposed, may control the rate of H_2O_2 production.

2. As noted in the main body of this report, not only is there light emission from stressed specimens, but there is a crack-like pattern of dark stains that appears on the specimen surface in the presence of the luminol-hemin-K_2CO_3 indicator. The onset of staining is, roughly speaking, at the 25% to 40% point in the fatigue life of specimens stressed to 35,000 psi ($\approx 100,000$-cycle lifetime). There is evidence that the crack stains develop as

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a result of exposure of the specimens to the basic (pH=11) solution, the stain color being darkened by hemin.

It is possible, then, that products of this presumed Al-K_2CO_3 reaction are deposited in cracks and that these deposits inhibit the access of water and oxygen to the clean crack surfaces, thus preventing the formation of H_2O_2 and reducing luminosity.

3. The oxidation of luminol to produce light output is a fairly complex reaction, particularly in the presence of such accelerators as hemin. In the process the accelerator is chemically reduced, thus being removed as an active agent. The loss rate of hemin is not known for experiments made by CAL; therefore, the significance of hemin loss as an influence in luminosity reduction cannot be judged.

4. As shown by Ojima (27), and as stated in this report, the luminous efficiency of the luminol solution is strongly dependent on pH, a value of 11.0 being close to optimum. If, as suggested in (2) above, an Al-K_2CO_3 reaction does take place, then it may be assumed that the solution's pH changes from its initial optimum value to one less favorable to the production of light output.

The above considerations, taken singly or in any combination, may well serve to qualify the observations represented in Figure 11.

In conclusion, one feature of chemiluminescent solutions as fatigue indicators should be noted: H_2O_2 must be produced at crack sites in the stressed specimens. The observed luminosity does not, however, appear just at those sites but is spread more or less throughout the solution. That fact suggests that H_2O_2 diffuses fairly readily within the solution, leading to luminosity wherever luminol molecules can be found. This behavior, together with that discussed above, suggests that while luminosity appears to indicate surface failure, measurements of luminosity cannot be made specifically sufficient either to isolate the crack sites or to serve as a guide to time-remaining-until-failure.

Fortunately, the overall TRIFFID work shows that other indicators offer somewhat more promise; their pursuit may be advantageous.

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13. ABSTRACT

The purpose of the study was to investigate, through laboratory tests, the potential for developing fatigue indicators for which some merit was evident from prior research. The response of photographic emulsions, phosphor coatings, and chemical indicator coatings to physical and surface-chemical reactions associated with fatigue damage in 2024-T3 aluminum was investigated. Many indicators were examined for their ability to meet the Army's requirements (1) under field conditions, (2) for long periods, and (3) for detection of damage that is characteristic of both high- and low-stress cycling. None of the candidate indicators was developed to a point where it showed promise for meeting these requirements during the contract period. Further investigation is recommended for one color indicator that was only briefly tested. Surface replication followed by microscopic examination was found to provide useful information on progressing fatigue damage. Effort directed toward developing practical methods for relating replica data to remaining life-to-failure is recommended.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fatigue						
Fatigue Testing						
Fatigue Indicator						
Fatigue Damage						
Exo-Electron						
Chemical Indicator						
Russell Photography						
Thin Film Replication						
Microscopy						
Metal Fatigue						
Fatigue Failure						

END